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ORIGINAL RESEARCH

Utilization of waste lignin to prepare controlled-slow release urea

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Abstract
Purpose The present work reports an economically attractive improvement in the area of producing particulate slow release nitrogen fertilizer using lignin as a waste effluent of pulp and paper manufacturing process.
Methods An improved coating of modified lignin was applied on the surfaces of the individual urea particles. The Kraft and Sulfite black liquors obtained from two different paper pulping units and were used as sources of sulfate and sulfite lignin, respectively. Chemical modification of extracted lignin was performed through acetylation reaction by acetic acid/sodium metabisulfite to increase its hydrophobicity character. In a separate experiment, a thin layer of synthesized acetylated lignin was coated on granular urea by fluidized-bed technique. The nitrogen release of synthesized fertilizer in the water and soil was examined by the Kjeldahl method.
Results The analysis of FTIR spectra indicated the changes in the functional groups of acetylated lignin. Petrographic photography and scanning electron microscopy (SEM) analyses demonstrated a uniform and homogeneous covering of the urea surface. The 7 day nitrogen release rate of urea coated by acetylated lignin in soil was obtained 36.3 and 45.3 % for Kraft and Sulfite lignin, respectively, whereas this value was 59 % for sulfur coated urea.
Conclusions Using industrial wastewater as source of lignin gives satisfactory results for industrial applications and yields a quality green fertilizer product with reduced operation difficulties while considerably preserving the environment.

Keywords Controlled release fertilizer · Fluidized-bed coating · Kraft and sulfite liquor · Modified lignin coated urea

Abbreviations

CRF	Controlled-release fertilizers
FTIR	Fourier transform infrared
SCU	Sulfur coated urea
SEM	Scanning electron microscopy

Introduction

The fertilizer industry faces a permanent challenge to improve the efficiency of its products. An ideal fertilizer should have at least three characteristics, including the needs for single application throughout the entire growing season; a high rate of return to the production input; and minimum detrimental effects on soil, water, and atmospheric environments (Shoji and Gandeza 1992; Trenkel 1997). Nitrogen is typically the most important nutrient in crop production in the world and used in the greatest amounts. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content. Unfortunately, due to its high water-solubility, it leads to ground water contamination particularly by nitrates through leaching processes. In addition, its rapid hydrolysis in soils results in a great quantity of nitrogen (30–50 %) running off and only a fraction is really absorbed by plants (Salman 1988; Malhi et al. 2001; Devassine et al. 2002; Ni et al. 2009; Da Rosa and dos Santos Rocha 2010). One possible way to reduce nitrogen losses and environmental

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pollution involves the use of controlled release urea in which a physical barrier is used to reduce its dissolution rate (Shavit et al. 2003). Controlled release urea is commonly prepared by coating of granular urea with low permeability hydrophobic material. Suitable coating must have four properties, including low prices, being biodegradable, non-toxicity, and high availability. It could effectively resolve and improve nutrient efficiency while reducing the environmental hazards (Shavit et al. 1997; Tomaszewska et al. 2002). Many materials have been reported to be used as coatings, such as sulfur, polyethylene, polysulfone, polyvinyl chloride, polystyrene, polyacrylic acid latex, chitosan, starch, polyvinyl alcohol, mixture of gypsum, limestone, cement, sulfur, and zeolite (Blouin et al. 1971; Salman 1989; Al-Zahrani 2000; Hanafi et al. 2000; Jarosiewicz and Tomaszewska 2003; Liang and Liu 2006; Lan et al. 2011; Mohd Ibrahim et al. 2014; Eghbali Babadi et al. 2015). The sulfur layer is friable and many works have reported the improvement of the coating quality using costly sealants and conditioners (Cole and Simmons 1992; Choi and Meisen 1997; Liu et al. 2008). Some of polymeric materials are non-biodegradable, toxic to the plants, and change the soil's pH, which is undesirable (Azeem et al. 2014). Recently, the development of bio-composite-based coating materials obtained from renewable sources has been investigated to obviate the disadvantages of non-biodegradability of certain polymer coatings and to offset higher operational costs (Calabria et al. 2012).

Lignin is a complex chemical compound and the only aromatic polymer present in wood and it is one of the most abundant biopolymers in nature (Glennie and McCarthy 1962). It is an amorphous polymer with a chemical structure that distinctly differs from the other macromolecular constituents of wood. Its chemical structure contains phenyl propane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl, and sinapyl alcohols (Dorrestijn et al. 2000; Boerjan et al. 2003). During the chemical pulping processes (Kraft, Soda and Sulphite), the partially degraded lignin is dissolved in the black liquor, from which it can be later isolated by different methods. Moreover, the molecular structure and function groups differ for the various types of lignin (Laurichesse and Avérous 2014). Lignin is a waste material that may be ideal for application to soil and is one of the most slowly decomposing components of dead vegetation, contributing a major fraction of the material that becomes humus as it decomposes. The resulting soil humus, in general, increases the photosynthetic productivity of plant. Moreover, this waste product, when embodied into soil, reduces the nitrification rate of urea (Stevenson 1982; Flaig 1984). Several systems, including urea and lignin, that used matrix method have been described for the formulation of slow release and decrease the solubility of urea. In one of these, urea was entrapped in a lignosulfonate-acrylonitrile graft copolymer matrix (Detroit 1988). Combinations of lignin and ethyl-cellulose were described as controlled release formulations of urea (Fernández-Pérez et al. 2008). The lignosulfonates, Kraft, and Soda lignins were used as coating material for production of coating urea. The nitrogen release through these coatings was measured and compared with uncoated urea granules. To reduce nitrogen release, hydrophobic compounds and crosslinkers were added to the soda flax lignin dispersions. However, complete release of nitrogen still occurred within 1 h (Mulder et al. 2011).

The objective of this work was to develop an economically feasible and biodegradable layer as coating material for urea fertilizer. For this purpose, lignin obtained from Kraft and Sulfite black liquor of pulp and paper industries was selected as raw material. The lignin with interesting functional properties was extracted and acetylated by acetic acid, and then served as coating layer.

Materials and methods

To improve the hydrophobicity property, acetylation reaction with acetic acid was used to modify sulfate and sulfite lignin. This approach is an environmentally friendly and cost-effective process with the advantages of using wastewater of pulp and paper mills. Figure 1 shows a schematic description of the experimental procedure.

Material

Black liquors from Kraft pulping of spruce (Choka Company. Anzali/Iran) and Sulfite process (Chokam Company, Mazandaran/Iran) were used as sources of sulfate and sulfite lignins, respectively. The granular urea was obtained from the Kermanshah Petrochemical Industries Company (Iran) which has a nitrogen content of 46.6 % and a particle size range of 2–4 mm (Table 1). Aqueous solution of acetic acid (5 %) containing sodium metabisulfite (0.2 %) was used as acetylating agents. Dichloromethane and ethanol (96 %) were used as the solvents for coating solution preparation. All chemicals were analytical grade (Merck; Germany) and used without further purification.

Methods

Extraction and chemical modification of lignin

Ultra-filtration of black liquor for the extraction of lignin has been studied in several previous investigations (Wallberg et al. 2003; Wallberg and Jönsson 2003; Holmqvist

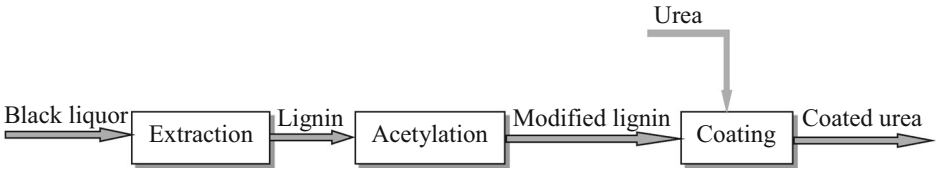

Fig. 1 Schematic description of the lignin modification and coating procedure

Table 1 Characterizations of raw materials used for preparation of controlled release urea

Materials	Amount	Unit
Urea granules		
Nitrogen content	46.6	wt%
Moisture content	0.3	wt%
Average diameter of the granules	3.0	mm
Molecular weight	50.6	g/gmol
Density	750	kg/m^3
Melting temperature	135	°C
Black liquor from Kraft pulping		
Lignin	43	wt%
Hydroxy acid	20	wt%
Sodium	18	wt%
Resin and fatty acids	6	wt%
Acetic acid	6	wt%
Formic acid	2	wt%
Hemicellulose and sugar	1	wt%
Other components	12	wt%
Black liquor from sulfite pulping		
Lignin	16	wt%
Hydroxy acid	24	wt%
Sodium	21	wt%
Resin and fatty acids	5	wt%
Acetic acid	11	wt%
Formic acid	2	wt%
Hemicellulose and sugar	2	wt%
Other components	19	wt%

et al. 2005; Wallberg et al. 2006). The lignin was extracted with a polymeric membrane, i.e., polyethersulfones (18 %) containing polyvinyl pyrrolidone(1 %) in a laboratory unit equipped with dead-end cell. Then, the extracted lignin was acetylated with acetic acid to block hydrophilic groups and improve coating properties, i.e., water sensitivity and hydrophobicity. Required amount of extracted lignin was acetylated under desired conditions, as shown in Table 2. The precipitated modified lignin was washed with 1 L deionized water and dried at 35–40 °C in an oven. The modified lignin was characterized through FTIR spectroscopy.

Coating of granular urea

Controlled release urea is commonly produced by the pan, rotary drum, and fluidized-bed coating techniques. The fluidized-bed process results in coatings of good quality and of uniform thickness (Tzika et al. 2003). Experimental setup, including the fluidized-bed coater and its accessories, is shown in Fig. 2. The fluidized bed was made of Pyrex column (20 cm in diameter and 40 cm in height). In each experimental run, granular urea (250 g) was loaded into fluidized-bed coater. The blower and pre-heater were run for 5–10 min to achieve a steady-state fluidization condition. Preliminary experiments were conducted before obtaining the optimum process variable of fluidization. The coating solution was prepared by dissolution of the extracted lignin or modified lignin powder in adequate solvent and sprayed into the granular urea via a nozzle. Deionized water was used as a solvent of extracted Kraft and Sulfite lignin, and a mixture of ethanol/dichloromethane was used as the solvent of modified lignin with acetic acid. Operating parameters of coating experiments are shown in Table 3. Spraying step was completed when a film of specified thickness was formed and the thickness of coated layer was controlled by regulating the coating period and coating solution flow rate. The coated granules were dried in the same apparatus at 70 °C for additional 10 min where after the granules were taken out for analysis. To prepare the sulfur coated urea, the sulfur was melted before being sprayed. Percentage of coating was determined as the weight of the modified lignin in the coating solution divided by the final weight of the product.

Characterization

The extracted lignin and modified lignins were characterized using Fourier Transform Infrared Spectroscopy (Bomem MB 155S series FTIR spectrophotometer;

Table 2 Experimental conditions of acetylation reaction of lignin

Reagent	Reactor	Time	Temperature	Centrifuging	Product
Acetic acid/sodium metabisulfite	Two necked flask with a condenser	18 h	80 °C	Four times, 60 min, 4000 rpm	Brown powder

Fig. 2 Experimental setup, including fluidized-bed apparatus

Table 3 Operating parameters of coating process in a fluidized bed

Process variable	Coating material		
	Lignin	Modified lignin	Sulfur
Weight of urea (g)	250	250	250
Air temperature (°C)	80–85	70–80	70–80
Air flow rate (cm^3/min)	35–45	35–45	35–45
Coating solution temperature (°C)	90–100	40–50	120–125
Coating solution flow rate (cm^3/min)	15	20	10
Coating solution pressure (bar)	15–18	15–18	15–18

Switzerland). Surface morphology of granular urea and modified lignin coated urea was analyzed by scanning electron microscopy (SEM) and petrographic microscopy (Leica 200M, USA). SEM images were obtained at the required magnification at room temperature.

Nitrogen release test

To measure the amount of nitrogen release in soil, synthesized fertilizer (3 g) was added to pot containing 900 g of soil, mixed, and kept at the room temperature of 25 ± 5 °C for 2 months. The humidity of pot's soil was controlled around field capacity by weighting method. Soil samples were collected from three different points in a 2 day interval by a narrow glass pipe with a diameter of 4 mm and height of 30 cm and subjected to nitrogen release test. The sampling points were isolated by the small-opening grid in the way that the samples only contained soil and none of synthesized slow release fertilizer beads.

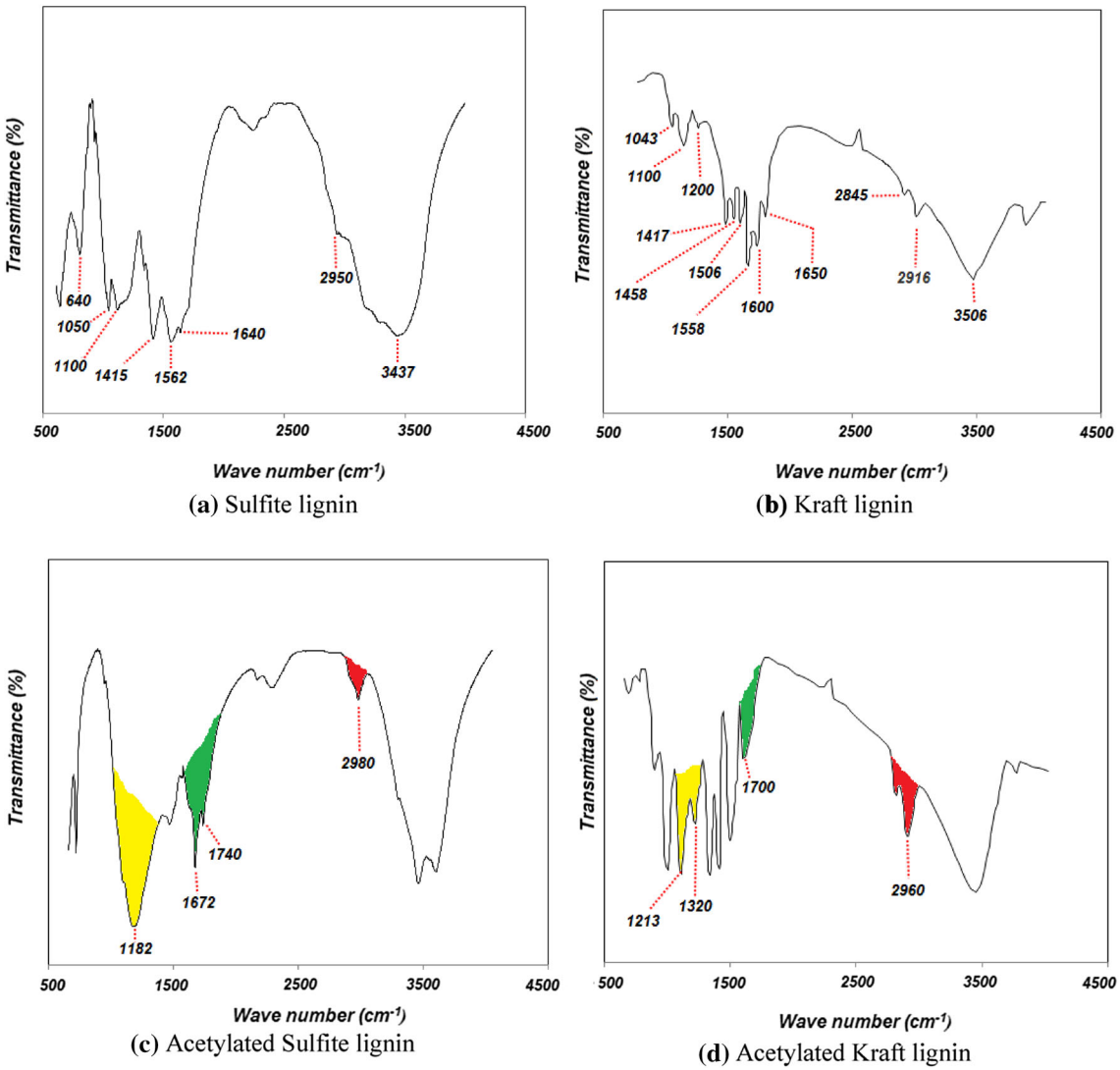

Fig. 3 FTIR spectra of extracted lignin and modified lignin

The nitrogen release rate of coated urea was measured by the Kjeldahl method using Gerhardt apparatus (James 1995). The Kjeldahl digestion converts nitrogen compounds into ammonia. One gram of sample (soil) is first digested in 10 ml strong sulfuric acid in the presence of 8 g catalyst (containing 96 % potassium sulfate, 3.5 % copper sulfate, and 0.5 % selenium dioxide) which helps in the conversion of the nitrogen to ammonium ions. This process was conducted at 250 °C for 30 min then at 410 °C for 50 min followed by the addition of water (100 ml) to the solution after settling the temperature to an ambient value. Ammonium ions were converted to ammonia by raising the temperature to boiling point and the ammonia was trapped in a solution of 10 ml Boric acid and Bromocresol green indicator. Then, nitrogen content was determined by titrating the ammonia solution with a standard solution of sodium hydroxide (0.05 N).

To measure the nitrogen release from fertilizer, a mass of 10 g coated urea was poured in deionized water (200 ml). Samples (10 ml) were withdrawn during intervals and subjected to the Kjeldahl method concluding the amount of nitrogen released from the fertilizer.

Results and discussion

Lignin macromolecule contains various functional groups, such as methoxyl, hydroxyl, and benzyl alcohol groups, and few terminal aldehyde groups (Nikitin 1961). The hydroxyl functional groups, mainly phenolic and alcoholic hydroxyl groups, may result in an increase hydrophilicity of lignin.

FTIR spectra of unmodified lignin extracted from black liquor and modified lignin are shown in Fig. 3. Some

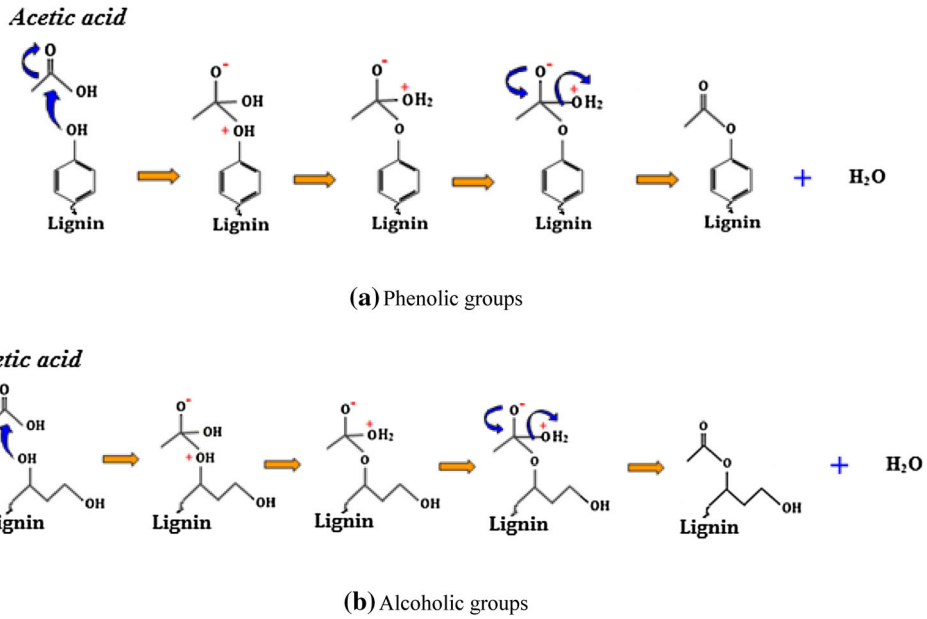

Fig. 4 Mechanism of the acetylation reaction with acetic acid/sodium metabisulfite. **a** Phenolic groups; **b** alcoholic groups

characteristic peaks in lignin spectrum can be ascribed as follows: The distinct band appearing at 640 cm^{-1} in the spectra of sulfite lignin (Fig. 3 a) was assigned to the sulphonic groups formed from the reaction of sodium sulphite with the secondary OH of the aliphatic side chain of lignin which is not the case in Kraft lignin spectrum. The bond at 1043–1200 cm^{-1} might be caused by vibration of C–O bonds in phenolic, alcoholic groups, and by vibration of C–O–C in ethers groups. The absorption bonds around 1050 and 1100 cm^{-1} are referred to primary and secondary alcoholic groups, respectively. The peaks at 1562 and 1640 cm^{-1} are related to the aromatic structural vibrations. The bond at 1650 cm^{-1} is due to stretching vibration of C=C in alkenes groups. The absorption bonds located in 2916 and 2845 cm^{-1} wave numbers are caused by C–H stretching vibration of the methoxyl groups. The strong wide absorption bond between 3100 and 3500 cm^{-1} is ascribed to OH stretching vibration, which indicates the presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds. The result of FTIR spectra confirmed that the precipitated material is extracted lignin which was hydrophilic because of existence many hydroxyl groups in its structure. Lower absorption intensity was observed for Kraft Lignin than for Sulfite lignin which is attributed to the high oxidation and degradation power during the two pulping processes (Fig. 3a, b).

The FTIR spectra of extracted lignin and modified lignin (Fig. 3c, d) show structural differences between them. The acetylation reaction has changed the structure of lignin when the main absorption bands (C=O) of acetyl groups have been appeared distinctly at 1700–1750 cm^{-1} that related to carboxylic acid group that formed by substitution of hydrogen atoms of the hydroxyl groups by acetyl groups. The new bond at 1195, 1213, and 1320 cm^{-1} in FTIR spectra of acetylated lignin is characteristic of C–O stretching vibration of esters and acidic groups. Meanwhile, the peak at 3100–3500 cm^{-1} of absorption is weakened after acetylation. Therefore, it can be concluded that hydroxyl groups in lignin were acetylated and replaced by acetyl groups. The absorption at 2934 cm^{-1}, predominantly, is due to C–H stretching in aromatic methoxyl groups. Increase of this peak intensity after modification by acetic acid is probably due to addition of methyl and methylene groups to side chains of acetylated lignin.

Figure 4 shows the proposed mechanism of acetylation reaction with acetic acid/sodium metabisulfite. A reaction involving the replacement of the hydrogen atom of a hydroxyl group with an acetyl group (CH_3CO) yields a specific ester. Acetylation of the lignin leads to a partial or full OH bond loss, since OH groups were replaced by ester groups (CH_3COO).

Figure 5a, b presents graphs and micrographs of the surface of uncoated urea and lignin coated urea (10 % coating) obtained by petrographic microscope and SEM. Lignin coated urea did not show a smooth surface, containing irregularities. In addition, crystal structure was observed on the particle surfaces of lignin coated urea. The formation of this crystal structure can be ascribed to phenolate salt crystal. Figure 5c shows the geological images (left) of acetylated lignins and SEM images (right) of urea coated with various percentage of acetylated Kraft lignin layer. Pinholes were clearly seen in samples with 5.0 % coating. These relatively large pinholes are the principal path for the water diffusion into coated granule and nitrogen

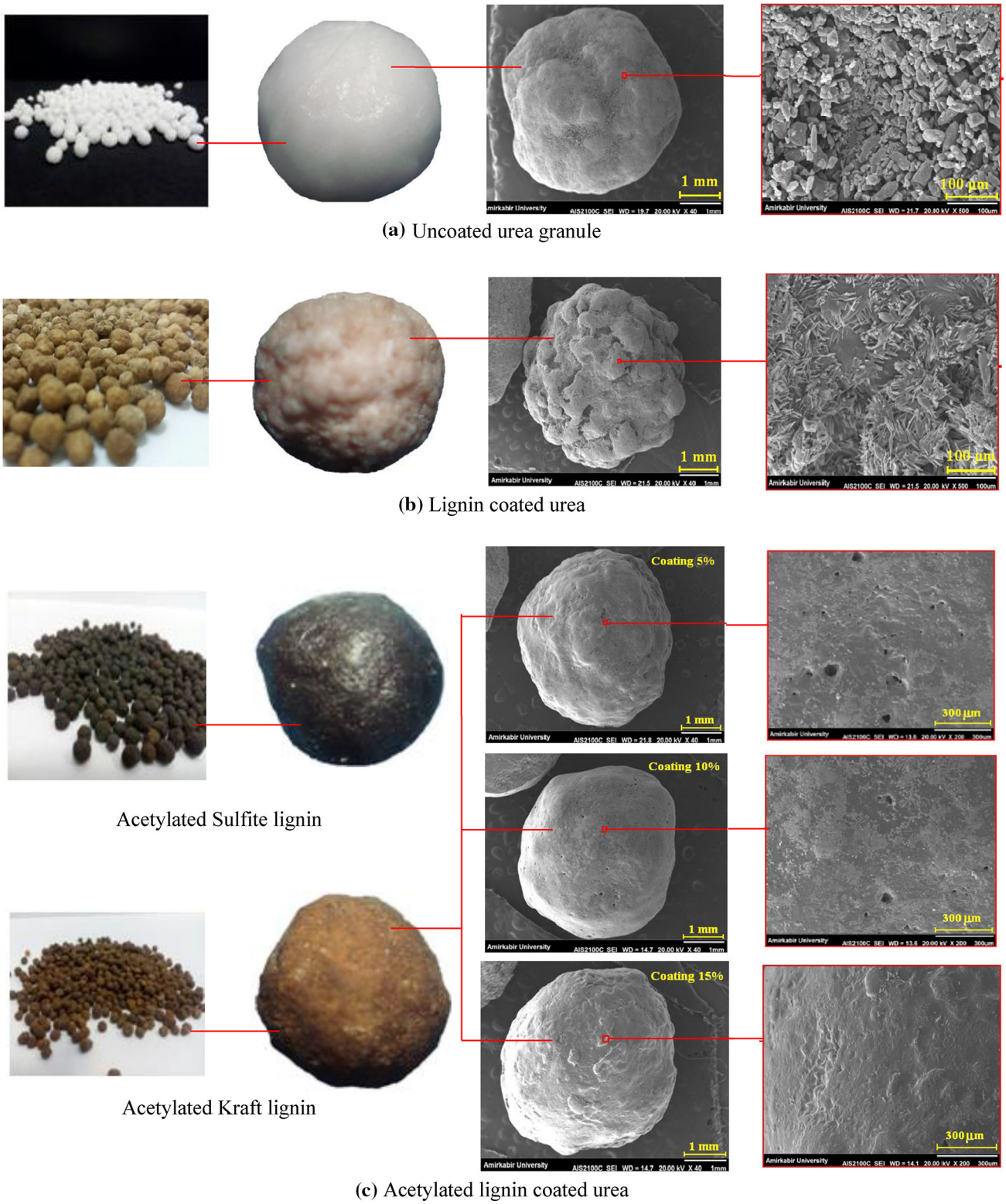

Fig. 5 Petrographic microscope and SEM images of urea, urea coated with lignin, and modified lignin with acetic acid. **a** Uncoated urea granule, **b** lignin coated urea, and **c** acetylated lignin coated urea

release. Nutrients become available when the coating degrades to expose them or when nutrients diffuse through small pores in the coating. Particles with thin or imperfect spots in the coating are covered by the sealant to moderate the release rate. The surface of the coated urea became more uniform and the pores sizes became smaller as the coating

percentage increased. Although the surface of the urea coated with 15.0 % coating was not perfectly uniform and smooth, it is quite free from visible defects like cracks and pinholes. The longest delay in release comes from the thicker coated particles with no imperfections. Thus, it is the variability in the particles that provides the sustained release of nutrients from coated urea.

Complete release of urea coated with Kraft and Sulfite lignin still occurred within 1 h in water. This can be explained by partly dissolution of urea in the aqueous lignin layer during coating process. The reaction of urea with phenolic hydroxyl groups of lignin results in the formation of phenolate salt in the coating layer; therefore, the coating layer has a low resistance to water diffusion.

Release of nitrogen is governed by the thickness of coating and imperfections in coating surface. Figure 6 shows nitrogen release rate of coated urea with modified lignin for three different coating percentages and in water medium. The release rate could be controlled by varying the total amount of coating layer. The dissolution rate decreases with the increase in coating percentage. For coated urea with acetylated Kraft lignin and Sulfite lignin, the dissolution rate of 88 and 97 % was obtained after 24 h for the sample with 5.0 % coating, respectively, whereas the corresponding value was 43 and 72 % for the sample with 15.0 % coating. This fact is associated with the reduction in the number of pinholes which are the primary path for nitrogen release from coated urea. It is important to note that higher the percentage content of coated layer results in lower release of nitrogen. For all experimental range, the nitrogen release for urea coated with acetylated Sulfite lignin was more than that of urea coated with acetylated Kraft lignin.

To achieve more practical results, the release rate of nitrogen was investigated in soil collected from agricultural farm in Kermanshah province/Iran (Fig. 7). The release rate of nitrogen was more slowly in soil than in water. However, the same trend was observed for acetylated Sulfite and Kraft lignin. Some of the physical and chemical properties of the soil are shown in Table 4.

To compare the quality of synthesized fertilizer with available commercial one, an experimental run was

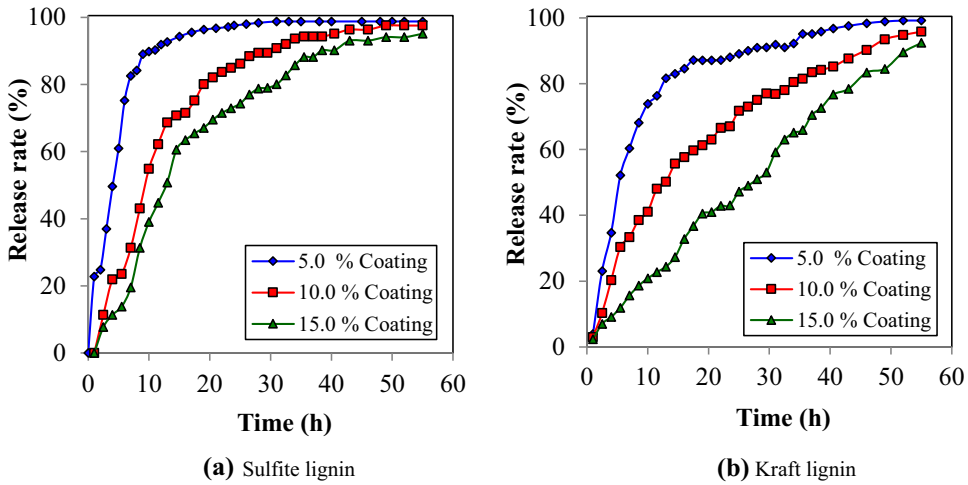

Fig. 6 Release rate of urea coated with acetylated lignin in water. **a** Sulfite lignin; **b** Kraft lignin

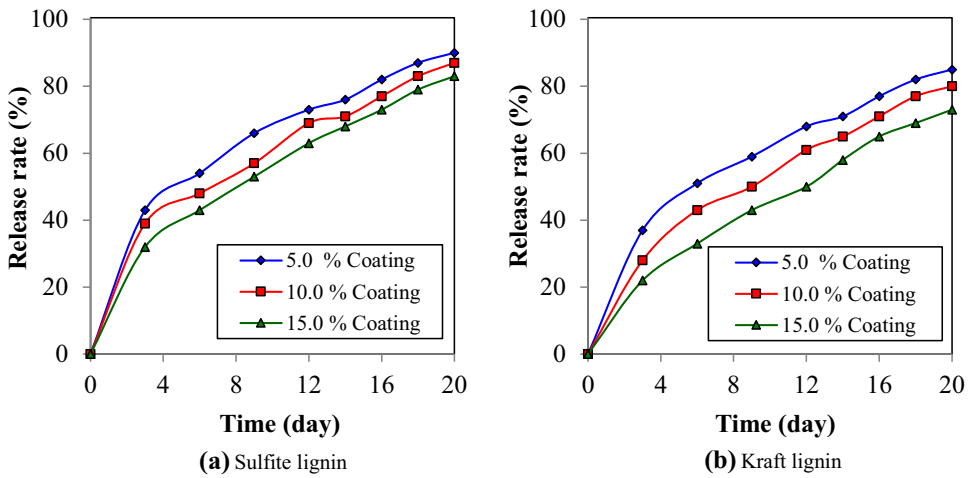

Fig. 7 Release rate of urea coated with acetylated lignin in soil. **a** Sulfite lignin; **b** Kraft lignin

Table 4 Properties of soil used for release rate of coated urea

Parameter	Value
pH	7.20
Electrical conductivity (ds/m)	0.40
Organic materials (%)	2.11
Nitrogen (%)	0.24
Calcium carbonate equivalent (%)	9.35
Silt (%)	55.17
Sand (%)	19.27
Clay (%)	25.56
Texture	Silt loam

conducted with sulfur coated urea (SCU) synthesized in our laboratory. Figure 8 illustrates the nitrogen release rate for SCU (without using conditioner and sealant) and urea coated by modified lignin for three different coating percentages. After 7 days, the nitrogen release of SCU in soil was more than urea coated with acetylated lignin. The nitrogen content of SCU has been released almost completely, after 11 days, whereas this value was 70 % (after 18 days) for the urea coated with acetylated Kraft lignin. This is probably due to complete coating of urea by acetylated lignin that prolonged the release time of nitrogen. The sulfur coating process is highly temperature dependent. A small change in coating temperature changes the morphology of sulfur. The sulfur cannot create a perfect-uniform coating on the surface of urea and some crack might be observed on the surface, which makes nitrogen release un-controllable. Moreover, some regions of the coating are thick and some regions are thin. The thinner part is easily broken and increases water penetration into granules that cause rapid dissolution of nitrogen.

For the application as a controlled release coating, the water resistance is an important feature. The dissolution rate of nitrogen reduced significantly for urea coated with modified lignin. Probably, acetylation increases the hydrophobicity and thereby reduces the water-sensitivity of lignin coating which results in a decrease of nitrogen release. In this coating layer, only some parts of the alcoholic and phenolic groups were acetylated and the others remained non-acetylated. Acetylated groups are characterized by hydrophobicity, while non-acetylated groups have the ability to establish hydrogen bonds with the coating surface, and thus, it can enhance the surface adhesion. FTIR spectra showed that Sulfite lignin is more hydrophilic than Kraft lignin. Due to its hydrophobic nature and adhesion to the surface, Kraft lignin modified with acetic acid/sodium metabisulfite showed the high performance as coating material (Fig. 9). Besides the hydrophobicity, the coating quality has the major influence on the release of urea. The fluidization is a suitable technique to produce a quality product with the uniform coating layer.

Conclusions

Extracted lignin from Kraft and Sulfite black liquor has the potential to be developed as a coating layer. Urea has been successfully coated with modified lignin to obtain granular coated urea. The key findings of this work are:

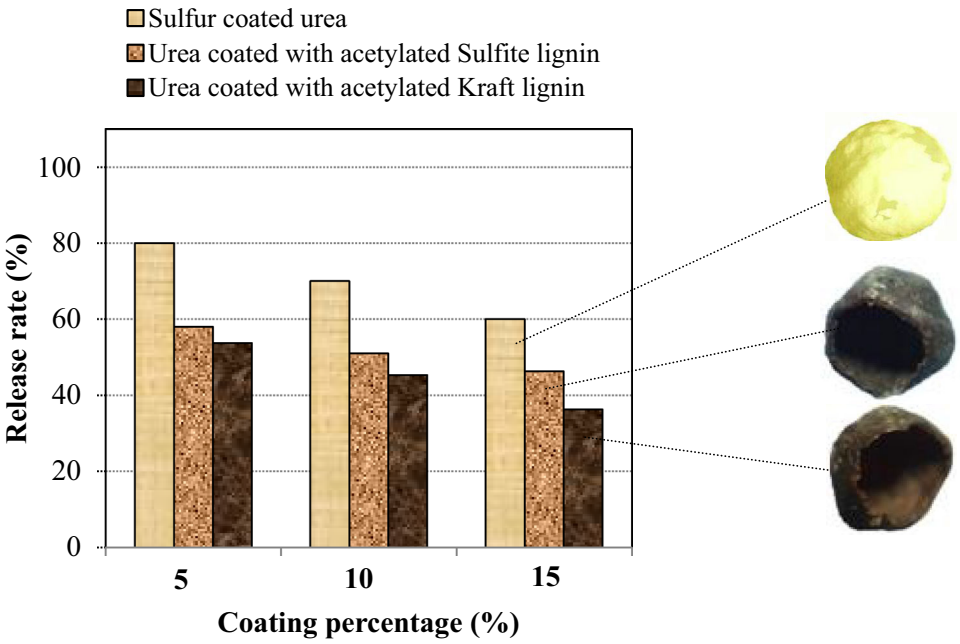

Fig. 8 Release rate of coated urea in soil after 7 days

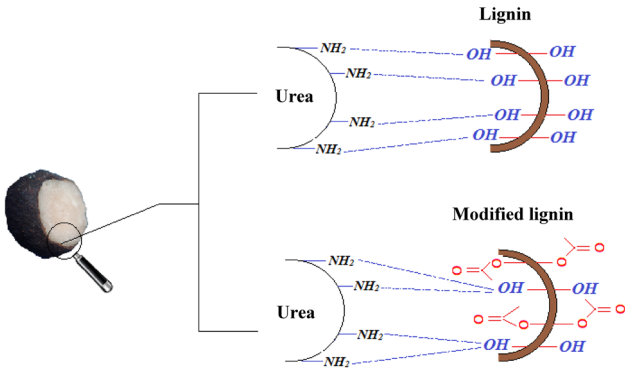

Fig. 9 Interface phenomenon between urea and coating agent

- The hydrophobic and adhesion surface characters of the coating material are two important factors affecting the quality of the coating and have a substantial influence on the nitrogen release. The hydrophobicity property of lignin layer was improved by its modification through acetylation reaction with acetic acid. The phenolic and alcoholic OH groups, which can be able to form hydrogen bond and increase its hydrophilic property, are converted to ester groups. However, adhesion surface characters of the coating decreased with an increase in coating hydrophobicity.
- The use of bio-polymeric materials, such as lignin, in controlled release fertilizer, could help to increase the efficiency of delivery of the bioactive material for longer period and prevent pollution of surface and underground water with nitrate.
- The existing environmental problems resulting from effluent of pulp and paper industries could be minimized by investments from both the fertilizer and the pulp/paper industries. This would result in economical and environmental benefits from the raw materials used in fertilizer industry.

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